

REPORT DOCUMENTATION PAGE			Form Approved OMB No. 0704-0188	
<small>Public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden, to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302, and to the Office of Management and Budget, Paperwork Reduction Project (0704-0188), Washington, DC 20503.</small>				
1. AGENCY USE ONLY (Leave blank)		2. REPORT DATE 20 December 1995		3. REPORT TYPE AND DATES COVERED Technical
4. TITLE AND SUBTITLE REACTIONS OF PHENYLALUMINIUM COMPOUNDS WITH E(SiMe <sub>3</sub> ) <sub>3</sub> (E = P or As): X-RAY CRYSTAL STRUCTURES OF Ph <sub>3</sub> Al-E(SiMe <sub>3</sub> ) <sub>3</sub> (E = P or As) AND Ph <sub>2</sub> (Cl)Al-P(SiMe <sub>3</sub> ) <sub>3</sub>			5. FUNDING NUMBERS •N00014-95-1-0194 R&T Project 3135008---16 •N00014-93-1-0860 R&T Project 4135008---13 •Dr. Harold E. Guard	
6. AUTHOR(S)  Janeen A. Laske Cooke, Hamid Rahbarnoohi, Andrew T. McPhail, Richard L. Wells*, and Peter S. White				
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)  Department of Chemistry Duke University Durham, NC 27708-0346			8. PERFORMING ORGANIZATION REPORT NUMBER Technical Report No. DU/DC/TR-52//AASERT-04	
9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES)  Office of Naval Research 300 North Quincy Street Arlington, VA 22217-5000			10. SPONSORING / MONITORING AGENCY REPORT NUMBER	
11. SUPPLEMENTARY NOTES  Accepted for Publication in <i>Polyhedron</i>				
12a. DISTRIBUTION / AVAILABILITY STATEMENT  Approved for Public Release Distribution Unlimited			12b. DISTRIBUTION CODE	
13. ABSTRACT (Maximum 200 words)  The independent reactions of Ph <sub>3</sub> Al with E(SiMe <sub>3</sub> ) <sub>3</sub> (E = P or As) in 1:1 mole ratios afforded the adducts Ph <sub>3</sub> Al•E(SiMe <sub>3</sub> ) <sub>3</sub> [E = P (I) and As (II), respectively]. The attempted dehalosilylation reactions between Ph <sub>2</sub> AlCl and E(SiMe <sub>3</sub> ) <sub>3</sub> (E = P or As) in 1:1 mole ratios yielded only the adducts Ph <sub>2</sub> (Cl)Al•E(SiMe <sub>3</sub> ) <sub>3</sub> [E = P (III) and As (IV)]. The adduct Ph(Cl) <sub>2</sub> Al•P(SiMe <sub>3</sub> ) <sub>3</sub> (V) was isolated from the reaction of equimolar amounts of PhAlCl <sub>2</sub> and P(SiMe <sub>3</sub> ) <sub>3</sub> . Compounds I-V were characterized by NMR spectroscopy and partial elemental analysis. In addition, the solid-state structures of I-III were determined by single-crystal X-ray analysis. Compound I crystallizes in the monoclinic space group <i>P</i> 2 <sub>1</sub> / <i>n</i> ( <i>C</i> <sub>2h</sub> <sup>5</sup> ), while II crystallizes in the triclinic space group <i>P</i> -1( <i>C</i> <sub>1</sub> ) <sup>1</sup> , each with two discrete molecules per asymmetric unit. Crystals of compound III belong to the orthorhombic space group <i>P</i> 2 <sub>1</sub> 2 <sub>1</sub> 2 <sub>1</sub> ( <i>D</i> <sub>2</sub> <sup>4</sup> ). Compounds I-III are the first structurally-characterized compounds to contain phenyl-substituted Al centres bonded to heavier pnictogen atoms.				
14. SUBJECT TERMS Aluminum, Arsenic, Phosphorus, Adduct Synthesis, Crystal Structure			15. NUMBER OF PAGES 28	
			16. PRICE CODE	
17. SECURITY CLASSIFICATION OF REPORT Unclassified	18. SECURITY CLASSIFICATION OF THIS PAGE Unclassified	19. SECURITY CLASSIFICATION OF ABSTRACT Unclassified	20. LIMITATION OF ABSTRACT Unlimited	

OFFICE OF NAVAL RESEARCH

Grant N00014-95-1-0194  
R&T Project 3135008---16  
and  
Grant N00014-93-1-0860  
R&T Project 4135008---13

Dr. Harold E. Guard

Technical Report No. DU/DC/TR-52//AASERT-04

**REACTIONS OF PHENYLALUMINIUM COMPOUNDS WITH  
E(SiMe<sub>3</sub>)<sub>3</sub> (E = P or As): X-RAY CRYSTAL STRUCTURES  
OF Ph<sub>3</sub>Al·E(SiMe<sub>3</sub>)<sub>3</sub> (E = P or As) AND Ph<sub>2</sub>(Cl)Al·P(SiMe<sub>3</sub>)<sub>3</sub>**

JANEEN A. LASKE COOKE, HAMID RAHBARNOOHI,  
ANDREW T. McPHAIL, RICHARD L. WELLS\*, AND PETER S. WHITE

Accession For	
NTIS	<input checked="" type="checkbox"/>
DTIC	<input type="checkbox"/>
Unannounced	<input type="checkbox"/>
Justification	
By	
Distribution/	
Availability Codes	
Dist	Avail and/or Special
A-1	

Accepted for Publication in *Polyhedron*

Duke University  
Department of Chemistry,  
P. M. Gross Chemical Laboratory  
Box 90346  
Durham, NC 27708-0346

20 December 1995

19960104 230

Reproduction in whole or in part is permitted for any purpose of the United States Government.

This document has been approved for public release and sale; its distribution is unlimited.

**REACTIONS OF PHENYLALUMINIUM COMPOUNDS WITH  
E(SiMe<sub>3</sub>)<sub>3</sub> (E = P or As): X-RAY CRYSTAL STRUCTURES OF  
Ph<sub>3</sub>Al·E(SiMe<sub>3</sub>)<sub>3</sub> (E = P or As) AND Ph<sub>2</sub>(Cl)Al·P(SiMe<sub>3</sub>)<sub>3</sub>**

**JANEEN A. LASKE COOKE, HAMID RAHBARNOOHI,  
ANDREW T. McPHAIL, and RICHARD L. WELLS\***

Department of Chemistry, Paul M. Gross Chemical Laboratory, Duke University,  
Durham, NC 27708, U.S.A.

**PETER S. WHITE**

Department of Chemistry, Venable Hall, University of North Carolina at Chapel Hill,  
Chapel Hill, NC 27514, U.S.A.

**Abstract** - The independent reactions of Ph<sub>3</sub>Al with E(SiMe<sub>3</sub>)<sub>3</sub> (E = P or As) in 1:1 mole ratios afforded the adducts Ph<sub>3</sub>Al·E(SiMe<sub>3</sub>)<sub>3</sub> [E = P (I) and As (II), respectively]. The attempted dehalosilylation reactions between Ph<sub>2</sub>AlCl and E(SiMe<sub>3</sub>)<sub>3</sub> (E = P or As) in 1:1 mole ratios yielded only the adducts Ph<sub>2</sub>(Cl)Al·E(SiMe<sub>3</sub>)<sub>3</sub> [E = P (III) and As (IV)]. The adduct Ph(Cl)<sub>2</sub>Al·P(SiMe<sub>3</sub>)<sub>3</sub> (V) was isolated from the reaction of equimolar amounts of PhAlCl<sub>2</sub> and P(SiMe<sub>3</sub>)<sub>3</sub>. Compounds I-V were characterized by NMR spectroscopy and partial elemental analysis. In addition, the solid-state structures of I-III were determined by single-crystal X-ray analysis. Compound I crystallizes in the monoclinic space group  $P2_1/n$  ( $C_{2h}^5$ ), while II crystallizes in the triclinic space group  $P\bar{1}$  ( $C_1^1$ ), each with two discrete molecules per asymmetric unit. Crystals of compound III belong to the orthorhombic space group  $P2_12_12_1$  ( $D_2^4$ ). Compounds I-III are the first structurally-characterized compounds to contain phenyl-substituted Al centres bonded to heavier pnictogen atoms.

---

\* Author to whom correspondence should be addressed.

In contrast to the significant collection of literature concerning reactions of aluminium alkyls and alkylaluminium halides with pnictogen compounds, there is a dearth of analogous studies with arylaluminium derivatives. Although the solid-state dimeric structure of triphenylaluminium,  $\text{Ph}_3\text{Al}$ , was reported nearly thirty years ago by Malone and McDonald,<sup>1</sup> the first structurally-characterized triarylaluminium-based complex did not appear in the literature until 1979 when Burlitch *et al.*<sup>2</sup> reported the triphenyl[( $\eta^5$ -cyclopentadienyl)dicarbonyliron]aluminate anion,  $[\text{Ph}_3\text{Al}-\text{Fe}(\text{CO})_2\text{Cp}]^-$ . It was more than ten years later that Robinson and co-workers reopened this area of organoaluminium chemistry with their synthesis and characterization of the aminophenylalane compounds,  $\text{Ph}_3\text{Al}\cdot\text{N}(\text{H})_2^t\text{Bu}^3$  and  $[\text{Ph}_2\text{AlN}(\text{H})\text{Ph}']_2$  ( $\text{Ph}'$  = biphenyl)<sup>4</sup>. The Oliver group has also recently reported an extensive series of mesitylaluminium compounds, including  $[\text{Mes}_2\text{Al}(\mu\text{-Cl})]_2$ ,<sup>5</sup>  $\text{Mes}_3\text{Al}\cdot(4\text{-picoline})(\text{C}_7\text{H}_8)_{0.5}$ ,<sup>5</sup>  $\text{Et}(\text{Mes})_2\text{Al}\cdot\text{THF}$ ,<sup>5</sup>  $\text{Mes}_2(\text{Cl})\text{Al}\cdot\text{THF}$ ,<sup>5</sup>  $[\text{Mes}_2\text{Al}(\mu\text{-SR})]_2$  ( $\text{R}$  = phenyl, benzyl)<sup>6</sup> and  $[\text{Mes}_2\text{Al}(\mu\text{-SeMe})]_2$ <sup>7</sup> ( $\text{Mes}$  = 2,4,6- $\text{Me}_3\text{C}_6\text{H}_2$ ). To date, only one compound containing an arylaluminium moiety bonded to a heavier group 15 atom has been characterized by X-ray diffraction techniques, and it is the unassociated aluminium monophosphide  $\text{Trip}_2\text{AlP}(1\text{-Ad})\text{SiPh}_3\cdot 0.5$  hexane ( $\text{Trip}$  = 2,4,6- $^i\text{Pr}_3\text{C}_6\text{H}_2$ , 1-Ad = adamantyl), which was reported by Power and co-workers in 1994.<sup>8</sup>

The limited research into the arylaluminium chemistry of pnictogen compounds led us to investigate the reactions of phenylaluminium species with silylpnictines. Previously, researchers in our laboratory studied dehalosilylation and salt-elimination reactions between silylpnictogen compounds and heavier group 13 phenyl-substituted reagents, which led to the isolation of several novel 13-15 compounds.<sup>9-12</sup> For example, the 2:1 reaction of  $\text{Ph}_2\text{GaCl}$  and  $\text{As}(\text{SiMe}_3)_3$  afforded the first gallium-arsenic mixed-bridge compound,  $\text{Ph}_2\text{Ga}\overline{\text{As}(\text{SiMe}_3)_2\text{Ga}(\text{Ph})_2\text{Cl}}$ .<sup>9</sup> The Ga-P analog,  $\text{Ph}_2\text{Ga}\overline{\text{P}(\text{SiMe}_3)_2\text{Ga}(\text{Ph})_2\text{Cl}}$ , was synthesized from a similar reaction of  $\text{Ph}_2\text{GaCl}$  and  $\text{P}(\text{SiMe}_3)_3$ .<sup>11</sup> Lithium salt-elimination reactions between equimolar amounts of  $\text{Ph}_2\text{MCl}$  ( $\text{M}$  = Ga or In) and  $\text{LiE}(\text{SiMe}_3)_2$  ( $\text{E}$  = As or P) yielded dimeric compounds of the type  $[\text{Ph}_2\text{ME}(\text{SiMe}_3)_2]_2$  ( $\text{M}$  = Ga,  $\text{E}$  = As<sup>9</sup>;  $\text{M}$  =

In, E = As<sup>12</sup>; and M = In, E = P<sup>12</sup>). The triphenylgallium Lewis acid-base adducts Ph<sub>3</sub>Ga•P(SiMe<sub>3</sub>)<sub>3</sub><sup>11</sup> and Ph<sub>3</sub>Ga•As(SiMe<sub>3</sub>)<sub>3</sub><sup>13</sup> have been prepared by the direct combination of Ph<sub>3</sub>Ga and E(SiMe<sub>3</sub>)<sub>3</sub> (E = P and As, respectively) and also by unique rearrangement reactions involving the monolithium salts, LiE(SiMe<sub>3</sub>)<sub>2</sub> (E = P and As, respectively). Herein, we report the synthesis and characterization of the phenylaluminum-pnictine compounds, Ph<sub>3</sub>Al•E(SiMe<sub>3</sub>)<sub>3</sub> [E = P (I) or As (II)], Ph<sub>2</sub>(Cl)Al•E(SiMe<sub>3</sub>)<sub>3</sub> [E = P (III) or As (IV)], and Ph(Cl)<sub>2</sub>Al•P(SiMe<sub>3</sub>)<sub>3</sub> (V).

## EXPERIMENTAL

### *Synthesis*

All reactions and manipulations were carried out under vacuum, in a Vacuum Atmospheres HE-493 Dri-Lab under an argon atmosphere, and under argon using standard Schlenk apparatus.<sup>14</sup> The <sup>1</sup>H and <sup>13</sup>C{<sup>1</sup>H} NMR spectra were obtained on a Varian XL-300 spectrometer at 300.0 and 75.4 MHz, respectively. <sup>27</sup>Al NMR spectra were acquired on a Varian Unity 500 spectrometer at 130.3 MHz. <sup>31</sup>P NMR spectra were obtained on either a Varian XL-300 (121.4 and 300.0 MHz, respectively) or a Varian Unity 500 (202.4 and 500.1 MHz, respectively) spectrometer. <sup>1</sup>H and <sup>13</sup>C{<sup>1</sup>H} spectra were referenced to TMS via the residual protons or carbons of deuterated benzene (δ 7.15 ppm and 128.0 ppm, respectively). <sup>27</sup>Al and <sup>31</sup>P NMR spectra were externally referenced to Al(NO<sub>3</sub>)<sub>3</sub> and 80% H<sub>3</sub>PO<sub>4</sub>, respectively, at δ 0.00 ppm. All solvents were appropriately dried and distilled under dry nitrogen. The compounds P(SiMe<sub>3</sub>)<sub>3</sub>,<sup>15</sup> and As(SiMe<sub>3</sub>)<sub>3</sub><sup>16,17</sup> were prepared by literature methods. Triphenylaluminum, Ph<sub>3</sub>Al, was prepared by the literature procedure.<sup>1</sup> AlCl<sub>3</sub> was purchased from Strem Chemical, Inc. and purified by sublimation prior to use. Ph<sub>2</sub>AlCl and PhAlCl<sub>2</sub> were prepared by the stoichiometric equilibration of AlCl<sub>3</sub> and Ph<sub>3</sub>Al<sup>1</sup> in toluene. Melting points (uncorrected) were obtained with a Thomas-

Hoover Uni-melt apparatus in flame-sealed capillaries. Elemental analyses were performed by E+R Microanalytical Laboratory, Inc., Corona, New York.

### **Ph<sub>3</sub>Al·P(SiMe<sub>3</sub>)<sub>3</sub> (I)**

Triphenylaluminium, Ph<sub>3</sub>Al, (0.39 g, 1.53 mmol), was placed in a 300 cm<sup>3</sup> round-bottomed screw-top flask, along with 30 cm<sup>3</sup> of toluene and a stir-bar. A toluene (30 cm<sup>3</sup>) solution of P(SiMe<sub>3</sub>)<sub>3</sub> (0.38 g, 1.53 mmol) was added to the Ph<sub>3</sub>Al solution. No immediate reaction was observed. The flask was immersed in a preheated oil bath (110 °C) and heated for 2 d to give a clear, colourless solution. Solvent was removed *in vacuo*, resulting in an off-white crystalline solid, which was recrystallized from toluene at -30 °C. After several days, colourless, X-ray-quality crystals were isolated from the toluene solution, were determined to be I (0.64 g, 82% yield), mp 184-204 °C (gradually melts to a yellow liquid). Anal. Calcd. (Found) for C<sub>27</sub>H<sub>42</sub>AlPSi<sub>3</sub>: C 63.73 (63.95), H 8.32 (8.37). <sup>1</sup>H NMR: δ 0.11 [d, Si(CH<sub>3</sub>)<sub>3</sub>, 27H, (J<sub>P-H</sub> = 4.85 Hz)], 7.33 (m, C<sub>6</sub>H<sub>5</sub>, 9H), 8.18 (m, C<sub>6</sub>H<sub>5</sub>, 6H). <sup>13</sup>C{<sup>1</sup>H} NMR: δ 3.15 [d, Si(CH<sub>3</sub>)<sub>3</sub>, (J<sub>P-C</sub> = 7.3 Hz)], 127.6, 128.0, 128.4, and 140.0 (s, C<sub>6</sub>H<sub>5</sub>). <sup>27</sup>Al NMR: δ 189.5 (br. s). <sup>31</sup>P NMR: δ -232.5 (s).

### **Ph<sub>3</sub>Al·As(SiMe<sub>3</sub>)<sub>3</sub> (II)**

In a manner similar to the preparation of I, Ph<sub>3</sub>Al (0.31 g, 1.20 mmol) and benzene (30 cm<sup>3</sup>) were added to a 200 cm<sup>3</sup> round-bottomed screw-top flask, equipped with a stir-bar. A solution of As(SiMe<sub>3</sub>)<sub>3</sub> (0.36 g, 1.21 mmol) in benzene (30 cm<sup>3</sup>) was added to the flask, resulting in partial dissolution of the Ph<sub>3</sub>Al. The flask was immersed in an oil bath preheated to 65 °C, and heated for 2 d, resulting in homogeneous yellow solution. The volatiles were removed *in vacuo*, leaving a yellowish semi-solid in the flask. The flask was taken into the dry box, where the product was recrystallized from toluene at -30 °C.

After several days, long, rectangular colorless crystals of **II**, suitable for X-ray crystallographic analysis, were isolated (0.51 g, 78.0% yield), mp 192 - 195 °C (slight decomposition to an orange solid was observed). Anal. Calcd. (Found) for  $C_{27}H_{42}AlAsSi_3$ : C 58.66 (58.43), H 7.66 (7.92).  $^1H$  NMR:  $\delta$  0.15 [s,  $Si(CH_3)_3$ , 27H], 7.34 (m,  $C_6H_5$ , 9H), 8.15 (m,  $C_6H_5$ , 6H).  $^{13}C\{^1H\}$  NMR:  $\delta$  3.22 [s,  $Si(CH_3)_3$ ], 127.5, 127.9, 128.5, and 139.7 (s,  $C_6H_5$ ).

### **$Ph_2(Cl)Al \cdot P(SiMe_3)_3$ (III)**

Diphenylaluminium chloride,  $Ph_2AlCl$  (0.22 g, 1.01 mmol),  $P(SiMe_3)_3$  (0.25 g, 1.01 mmol), and hexane (75 cm<sup>3</sup>) were combined in a 250 cm<sup>3</sup> round-bottomed screw-top flask, equipped with a stir-bar. The resultant solution was turbid at room temperature, due to the limited solubility of  $Ph_2AlCl$  in hexane. The flask was then immersed in an oil bath, preheated to 65 °C, and heated for 2 d during which time, the solution became clear and colourless. The volatiles were then removed *in vacuo*, yielding an off-white solid product. The flask was taken into the dry-box, where the solid was recrystallized from pentane at -30 °C. Needle-like, colourless, X-ray-quality crystals were isolated and determined to be **III** (0.37 g, 78% yield), mp 141-155 °C (decomposes to a glassy yellow solid before melting). Anal. Calcd. (Found) for  $C_{21}H_{37}AlPClSi_3$ : C 53.99 (53.87), H 7.98 (7.89), Al 5.78 (5.62), P 6.63 (6.38), Cl 7.59 (7.48).  $^1H$  NMR:  $\delta$  0.17 [d,  $Si(CH_3)_3$ , 27H, ( $J_{P-H}$  = 5.10 Hz)], 7.31 (m,  $C_6H_5$ , 9H), 8.23 (m,  $C_6H_5$ , 6H).  $^{13}C\{^1H\}$  NMR:  $\delta$  2.71 [d,  $Si(CH_3)_3$ , ( $J_{P-C}$  = 7.9 Hz)], 127.5, 128.5, 129.0, and 138.6 (s,  $C_6H_5$ ).  $^{27}Al$  NMR:  $\delta$  181.6 (br. s).  $^{31}P$  NMR:  $\delta$  -225.2 (s).

### **Ph<sub>2</sub>(Cl)Al•As(SiMe<sub>3</sub>)<sub>3</sub> (IV)**

Inside a dry-box, a 250 cm<sup>3</sup> round-bottomed screw-top flask, equipped with a stir-bar, was charged with Ph<sub>2</sub>AlCl (0.26 g, 1.20 mmol) and 25 cm<sup>3</sup> of toluene, resulting in a colourless solution. A solution of As(SiMe<sub>3</sub>)<sub>3</sub> (0.35 g, 1.20 mmol) in toluene (30 cm<sup>3</sup>) was then added to the flask. The solution was immersed in a preheated oil bath (75 °C) and warmed for 1 d, during which time, the solution remained clear and colourless. After 24 h, the flask was removed from the oil bath and cooled to room temperature for 8 h, but no crystallization or precipitation of a solid product occurred. Volatiles were then stripped *in vacuo*, leaving an off-white crystalline solid, **IV** (0.49 g, 81% yield), which was washed with pentane, then dried, mp 131-135 °C (becomes a cloudy liquid), 138-140 °C (melts to a yellow liquid). X-ray quality single crystals of **IV** were unobtainable from repeated attempts at recrystallization. Anal. Calcd. (Found) for C<sub>21</sub>H<sub>37</sub>AlAsClSi<sub>3</sub>: C 49.35 (49.27), H 7.29 (7.18). <sup>1</sup>H NMR: δ 0.19 [s, Si(CH<sub>3</sub>)<sub>3</sub>, 27H], 7.31 (m, C<sub>6</sub>H<sub>5</sub>, 9H), 8.18 (m, C<sub>6</sub>H<sub>5</sub>, 6H). <sup>13</sup>C{<sup>1</sup>H} NMR: δ 3.00 [s, Si(CH<sub>3</sub>)<sub>3</sub>], 123.8, 127.6, 137.7, 138.4 and 139.7 (s, C<sub>6</sub>H<sub>5</sub>).

### **Ph(Cl)<sub>2</sub>Al•P(SiMe<sub>3</sub>)<sub>3</sub> (V)**

In the dry box, a mixture of PhAlCl<sub>2</sub> (0.48 g, 2.74 mmol) and benzene (40 cm<sup>3</sup>) was added to a 250 cm<sup>3</sup> round-bottomed screw-top flask, equipped with a stir-bar. To this was added a colourless solution of P(SiMe<sub>3</sub>)<sub>3</sub> (0.69 g, 2.74 mmol) in benzene (30 cm<sup>3</sup>). The resultant solution was turbid at room temperature, and a white solid began to precipitate. The reaction solution was immersed in an oil bath, preheated to 60 °C, and heated for 2 d during which time, the solution remained colourless with a white precipitate. The volatiles were then removed *in vacuo*, yielding a white solid product. The wash solution was decanted and transferred to a vial, then refrigerated at -30 °C. The solid was

recrystallized from hexane and pentane to give a white crystalline solid, **V** (1.03 g, 88% yield), no mp observed: 140-145 °C, colorless liquid condensed at the top of the capillary; 145-300 °C, decomposed to a yellow solid. Anal. Calcd. (Found) for  $C_{15}H_{32}AlPCl_2Si_3$ : C 42.34 (42.58), H 7.58 (7.30).  $^1H$  NMR:  $\delta$  0.26 [d,  $Si(CH_3)_3$ , 27H, ( $J_{P-H}$  = 5.07 Hz)], 7.25 (m,  $C_6H_5$ , 9H), 7.76 (br. s,  $C_6H_5$ ), and 8.06 (m,  $C_6H_5$ , 6H).  $^{13}C\{^1H\}$  NMR:  $\delta$  2.02 and 2.38 [d,  $Si(CH_3)_3$ , ( $J_{P-C}$  = 8.4 and 8.2 Hz, respectively)], 128.5, 129.0, 130.3, 130.6 and 138.1 (s,  $C_6H_5$ ).  $^{31}P$  NMR:  $\delta$  -220.1 (s).

#### *X-ray structural solution and refinement*

Crystallographic data for **I**, **II**, and **III** are summarized in Table 1. The X-ray crystal structure analysis of **I** was performed at the University of North Carolina-Chapel Hill Single-Crystal X-Ray Facility. A crystal of **I** was affixed to the end of a glass fibre using a viscous oil under a flow of nitrogen. Intensity data were recorded at -130 °C using the  $\omega$  scan mode on a Rigaku AFC6/S diffractometer [graphite monochromated Mo- $K\alpha$  radiation ( $\lambda$  = 0.71073 Å)]. Intensity data were corrected for absorption using  $\psi$ -scans. Refined unit-cell parameters were obtained from the diffractometer setting angles for 84 reflections ( $15^\circ < \theta < 20^\circ$ ) widely separated in reciprocal space. The space group  $P2_1/n$  was established uniquely from the Laue symmetry and systematic absences:  $0k0$  when  $k \neq 2n$ ,  $h0l$  when  $h + l \neq 2n$ . The asymmetric unit consists of two crystallographically-independent formula units. The crystal structure was solved by direct methods. Non-hydrogen atom positional and thermal parameters were refined using full-matrix least-squares adjustment techniques. In the final iterations, hydrogen atoms were incorporated at their calculated positions using a riding model, with parameter refinement converging at  $R$  = 0.048 ( $R_w$  = 0.051). Crystallographic calculations were performed on a DEC 3000/400 computer using the NRCVAX suite of structure-determination programs.<sup>18</sup> Neutral atom scattering factors and their anomalous dispersion corrections were taken from reference 19.

X-ray crystallographic analyses of **II** and **III** were performed at the Duke University Structure Centre. For X-ray measurements, crystals were mounted inside thin-walled glass capillaries, temporarily sealed with grease and then flame-sealed. Intensity data were collected at ambient temperature on an Enraf-Nonius CAD-4 diffractometer [graphite-monochromated Cu-K $\alpha$  radiation ( $\lambda = 1.5418 \text{ \AA}$ )]. Refined unit-cell parameters for each were derived from the diffractometer setting angles for 25 reflections ( $36^\circ < \theta < 40^\circ$ ) widely separated in reciprocal space. Intensity data were corrected for the usual Lorentz and polarization effects; empirical absorption corrections, based on the  $\phi$ -dependency of the intensities of several reflections with  $\chi$  ca.  $90^\circ$ , were also applied.

Laue symmetry indicated that crystals of **II** were triclinic, space group  $P1$  or  $P\bar{1}$ ; the latter was assumed at the outset and shown to be correct by the structure solution and refinement. The asymmetric unit consists of two crystallographically-independent formula units. The crystal structure was solved by direct methods (MULTAN11/82). Initial coordinates for the Al, As, and Si atoms were obtained from an  $E$ -map. A series of weighted  $F_o$  and difference Fourier syntheses yielded positions for the other non-hydrogen atoms. Positional and thermal parameters of the non-hydrogen atoms (at first isotropic, then anisotropic) were adjusted by means of several rounds of full-matrix least-squares calculations. Hydrogen atoms were incorporated at their calculated positions and an extinction correction was included as a variable in the final least-squares iterations which converged at  $R = 0.040$  ( $R_w = 0.053$ ). A final difference Fourier synthesis contained no unusual features.

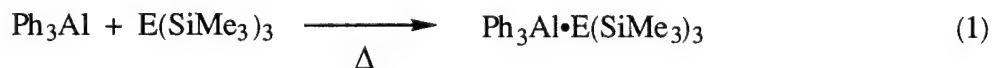
The space group for **III** was established uniquely as  $P2_12_12_1$  by the systematic absences:  $h00$  when  $h \neq 2n$ ,  $0k0$  when  $k \neq 2n$ ,  $00l$  when  $l \neq 2n$ . Coordinates for the isomorphous Ga analogue<sup>11</sup> were used as initial input to the structure-factor calculations. Several rounds of full-matrix least-squares refinement of positional and anisotropic thermal parameters of these atoms, with hydrogen atoms incorporated at their calculated positions in the later iterations, converged at  $R = 0.0473$  ( $R_w = 0.0661$ ). The polarity of the crystal

used for data collection was then established by introduction of the imaginary contributions to the anomalous dispersion corrections into the structure-factor calculations. For the parameters corresponding to those of the Ga analogue,  $R$  was 0.0501 while  $R_w$  was 0.0703, whereas values of  $R = 0.0464$  and  $R_w = 0.0648$  were obtained for those of the mirror image. The differences<sup>20</sup> indicated that the polarity had to be reversed. Continuation of the least-squares refinement led to convergence at  $R = 0.046$  ( $R_w = 0.064$ ). No unusual features were present in a final difference Fourier synthesis.

Crystallographic calculations for **II** and **III** were performed on PDP11/44 and MicroVAX computers by use of the Enraf-Nonius Structure Determination Package (SDP). For all structure-factor calculations, neutral atom scattering factors and their anomalous dispersion corrections were taken from reference 19.

## RESULTS AND DISCUSSION

The independent reactions of  $\text{Ph}_3\text{Al}$  with  $\text{P}(\text{SiMe}_3)_3$  and  $\text{As}(\text{SiMe}_3)_3$  in 1:1 mole ratios afforded the Lewis acid-base adducts  $\text{Ph}_3\text{Al}\cdot\text{P}(\text{SiMe}_3)_3$  (**I**) and  $\text{Ph}_3\text{Al}\cdot\text{As}(\text{SiMe}_3)_3$  (**II**), respectively (Eqn. 1).



$\text{E} = \text{P}$  (**I**), Toluene, 110 °C

$\text{E} = \text{As}$  (**II**), Benzene, 65 °C

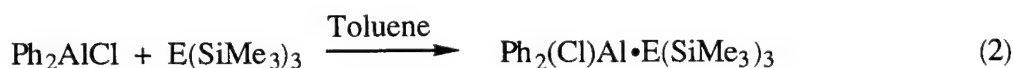
Adduct **I** is the aluminium analogue of the gallium-phosphorus adduct  $\text{Ph}_3\text{Ga}\cdot\text{P}(\text{SiMe}_3)_3$ ,<sup>11</sup> and it is only the second triarylaluminium-phosphorus compound to be structurally characterized. Compound **II**, the Al analogue of  $\text{Ph}_3\text{Ga}\cdot\text{As}(\text{SiMe}_3)_3$ ,<sup>13</sup> is only the third example of an Al-As adduct to be reported and it is the first arylaluminium-arsenic compound to be characterized by X-ray crystallographic analysis.

Both of the isostructural triphenylaluminium-pnicogen adducts  $\text{Ph}_3\text{Al}\cdot\text{P}(\text{SiMe}_3)_3$  (**I**) and  $\text{Ph}_3\text{Al}\cdot\text{As}(\text{SiMe}_3)_3$  (**II**) have unit cells that contain two crystallographically-independent, but virtually structurally identical, molecules in the asymmetric crystal unit. The same phenomenon was previously encountered in the crystal structures of the respective Ga analogues of **I** and **II**, viz.  $\text{Ph}_3\text{Ga}\cdot\text{P}(\text{SiMe}_3)_3$ <sup>11</sup> and  $\text{Ph}_3\text{Ga}\cdot\text{As}(\text{SiMe}_3)_3$ .<sup>13</sup> Crystals of the arylaluminium monophosphide,  $\text{Trip}_2\text{AlP}(\text{1-Ad})\text{SiPh}_3\cdot 0.5$  hexane, were also found to contain two discrete monomers in the asymmetric unit.<sup>8</sup> ORTEP<sup>21</sup> diagrams showing the solid-state conformations and atom numbering schemes of one of the unique molecules of **I** and **II** are given in Figs. 1 and 2, respectively; selected bond distances and angles are listed in Tables 2 and 3.

Crystals of **I** belong the monoclinic system, space group  $P2_1/n$ , and they are isomorphous with those of the gallium analogue,  $\text{Ph}_3\text{Ga}\cdot\text{P}(\text{SiMe}_3)_3$ .<sup>11</sup> The Al and P atoms in the pair of crystallographically-independent molecules have similar pseudotetrahedral coordination geometries. There are small, but significant, differences between corresponding pairs of angles (see Table 3). The Al-C and P-Si bonds are rotated by slightly different amounts from an eclipsed orientation about the Al-P bonds (mean  $26.5^\circ$  and  $24.7^\circ$ ) in each of the molecules; corresponding values in  $\text{Ph}_3\text{Ga}\cdot\text{P}(\text{SiMe}_3)_3$ <sup>11</sup> are  $25.5^\circ$  and  $23.2^\circ$ . The Al-P bond lengths at 2.514(2) and 2.521(2) Å in the independent molecules of **I** lie well within the observed range for other monodentate Al-P adducts [2.391(6) - 2.585(2) Å].<sup>22-30</sup> The distances in **I** are longer than those found in other alkylhaloaluminium-silylphosphine adducts:  $\text{Et}(\text{Cl})_2\text{Al}\cdot\text{P}(\text{SiMe}_3)_3$  [2.435(3) Å],<sup>29</sup>  $i\text{Bu}_2(\text{Cl})\text{Al}\cdot\text{P}(\text{SiMe}_3)_3$  [2.504(3) Å],<sup>29</sup>  $\text{Cl}_3\text{Al}\cdot\text{P}(\text{SiMe}_3)_3\cdot\text{Toluene}$  [2.392(4) Å],<sup>30</sup> and  $\text{Br}_3\text{Al}\cdot\text{P}(\text{SiMe}_3)_3\cdot\text{Toluene}$  [2.391(6) Å]<sup>30</sup>. The bond lengthening in **I** can be attributed to a decrease in the Lewis acidity of the  $\text{Ph}_3\text{Al}$  moiety versus the other Al-containing species. The only reported, shorter Al-P bond length in an arylaluminium-phosphorus compound is that at 2.342(2) Å in  $\text{Trip}_2\text{AlP}(\text{1-Ad})\text{SiPh}_3\cdot 0.5$  hexane where the Al centre has a three-coordinate trigonal planar geometry.<sup>8</sup>

The novel triphenylaluminium-arsenic adduct **II** crystallizes in the triclinic system, space group  $P\bar{1}$  with two crystallographically-independent molecules in the asymmetric unit. Although it is isostructural with the Ga-As analogue  $\text{Ph}_3\text{Ga}\cdot\text{As}(\text{SiMe}_3)_3$ ,<sup>13</sup> the crystals are not isomorphous. In common with the metal and pnictogen atoms in **I**,  $\text{Ph}_3\text{Ga}\cdot\text{P}(\text{SiMe}_3)_3$ , and  $\text{Ph}_3\text{Ga}\cdot\text{As}(\text{SiMe}_3)_3$ , the coordination geometry about the Al and As centres in both molecules of **II** is pseudotetrahedral. The C-Al-C angles in **II** [ $112.4(2)^\circ$  -  $115.0(2)^\circ$ ] are consistently larger than the C-Al-As angles [ $102.9(1)^\circ$  -  $105.5(1)^\circ$ ] whereas the Si-As-Si angles [ $104.77(4)^\circ$  -  $106.78(4)^\circ$ ] are smaller than the Al-As-Si angles [ $111.88(4)^\circ$  -  $113.37(5)^\circ$ ]. This pattern is similar to that in the Al-P analogue **I** [C-Al-C:  $110.5(2)^\circ$  -  $114.5(2)^\circ$  > C-Al-P:  $104.6(2)^\circ$  -  $107.2(2)^\circ$ ; Si-P-Si:  $105.7(1)^\circ$  -  $107.0(1)^\circ$  > Al-P-Si:  $110.1(1)^\circ$  -  $114.1(1)^\circ$ ] as well as in  $\text{Ph}_3\text{Ga}\cdot\text{P}(\text{SiMe}_3)_3$  [C-Ga-C:  $111.8(8)^\circ$  -  $116.2(8)^\circ$  > C-Ga-P:  $103.7(6)^\circ$  -  $107.3(6)^\circ$ ; Si-P-Si:  $104.9(3)^\circ$  -  $107.0(3)^\circ$  > Ga-P-Si:  $110.7(2)^\circ$  -  $114.3(2)^\circ$ ] and  $\text{Ph}_3\text{Ga}\cdot\text{As}(\text{SiMe}_3)_3$  [C-Ga-C:  $111.2(8)^\circ$  -  $115.7(4)^\circ$  > C-Ga-As:  $103.3(2)^\circ$  -  $106.0(2)^\circ$ ; Si-As-Si:  $104.9(1)^\circ$  -  $106.6(1)^\circ$  > Ga-As-Si:  $110.74(7)^\circ$  -  $114.45(7)^\circ$ ]. The Al-C and As-Si bonds are rotated by different amounts from an eclipsed orientation about the Al-As bonds in each of the molecules (mean  $29.0^\circ$  and  $23.3^\circ$ ). The corresponding Al-As bond lengths at  $2.598(1) \text{ \AA}$  and  $2.613(1) \text{ \AA}$  are significantly longer than those in the only other structurally-characterized Al-As adducts,  $i\text{Bu}_2(\text{Cl})\text{Al}\cdot\text{As}(\text{SiMe}_3)_3$ <sup>31</sup> [ $2.573(1) \text{ \AA}$ ] and  $\text{Cl}_3\text{Al}\cdot\text{As}(\text{SiMe}_3)_2\cdot(\text{C}_7\text{H}_8)$ <sup>32</sup> [ $2.463(2) \text{ \AA}$ ] with the longer distance in **II** being associated with the more nearly eclipsed conformer.

In an effort to prepare aluminium-pnictogen compounds containing either  $\overline{\text{Al-E-Al-E}}$  or  $\overline{\text{Al-E-Al-Cl}}$  (E = P or As) core rings by the elimination of  $\text{Me}_3\text{SiCl}$ ,  $\text{Ph}_2\text{AlCl}$  was allowed to react with  $\text{E}(\text{SiMe}_3)_3$  in a 1:1 mole ratio. The reactions yielded adducts  $\text{Ph}_2(\text{Cl})\text{Al}\cdot\text{P}(\text{SiMe}_3)_3$  (**III**) and  $\text{Ph}_2(\text{Cl})\text{Al}\cdot\text{As}(\text{SiMe}_3)_3$  (**IV**), rather than the condensation products of dehalosilylation (Eqn. 2).



E = P (**III**), 110 °C

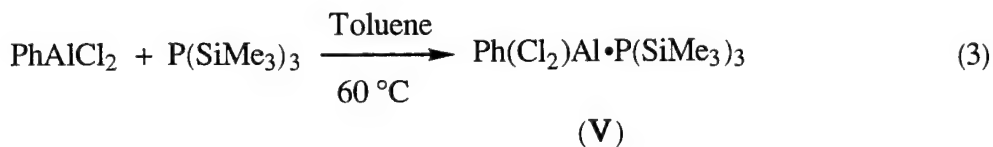
E = As (**IV**), 75 °C

Several attempts were made to recrystallize **IV**, but X-ray quality single crystals were not obtained.  $^1\text{H}$ ,  $^{13}\text{C}\{^1\text{H}\}$  NMR spectra and partial elemental analysis (*vide supra*) are consistent with an adduct having the formula  $\text{Ph}_2(\text{Cl})\text{Al}\cdot\text{As}(\text{SiMe}_3)_3$  (**IV**), which is the arsenic analogue of compound **III**.

An ORTEP<sup>21</sup> diagram showing the solid-state conformation and atom numbering scheme of **III** is presented in Fig. 3; selected bond distances and angles are listed in Table 4. In contrast to the triphenylaluminium-pnicogen adducts **I** and **II**, compound **III** crystallizes with only one molecule in the asymmetric unit of an orthorhombic unit cell (space group  $P2_12_12_1$ ). Crystals of **III** are isomorphous with those of the Ga analogue,  $\text{Ph}_2(\text{Cl})\text{Ga}\cdot\text{P}(\text{SiMe}_3)_3$ .<sup>11</sup> The Al and P atoms in **III** have the expected four-coordinate, distorted tetrahedral coordination geometries. The Al-P bond length at 2.467(2) Å lies well within the range of other aluminium-phosphorus monodenate adducts wherein the corresponding distances range from 2.391(6) to 2.585(2) Å.<sup>22-29</sup> Consistent with the increased Lewis acidity of  $\text{Ph}_2\text{AlCl}$  over the  $\text{Ph}_3\text{Al}$  moiety as a consequence of replacement of a phenyl substituent by a more electronegative Cl atom as well as the greater degree of rotation from an eclipsed conformation, the Al-P bond in **III** is noticeably shorter than those in **I** [2.514(2), 2.521(2) Å].

When equimolar amounts of  $\text{PhAlCl}_2$  and  $\text{P}(\text{SiMe}_3)_3$  were allowed to react in benzene at 60 °C, a white solid immediately precipitated out of solution (Eqn. 3). Titration of the volatiles collected from the reaction flask revealed that no  $\text{Me}_3\text{SiCl}$  was eliminated during the course of the reaction. Several attempts at recrystallization of the white solid product were made; however, X-ray quality single crystals were unobtainable.  $^1\text{H}$ ,

$^{13}\text{C}\{^1\text{H}\}$  NMR spectra and partial elemental analysis of the product are consistent with a 1:1 Lewis acid-base adduct structure,  $\text{Ph}(\text{Cl})_2\text{Al}\cdot\text{P}(\text{SiMe}_3)_3$  (**V**), as shown in Eqn. 3.



Analogous reaction of  $\text{PhAlCl}_2$  and  $\text{As}(\text{SiMe}_3)_3$  under similar conditions (Eqn. 3) gave a brown intractable solid which was insoluble in aromatic solvents and THF, and was not further investigated.

$^1\text{H}$ ,  $^{13}\text{C}\{^1\text{H}\}$  NMR spectra for compounds **I-V** are consistent with their formulation as adducts. The  $^1\text{H}$  NMR spectra for **I-V** contain two multiplets in the phenyl region, consistent with mono-substituted phenyl rings. The observed phenyl proton signals for **I-V** have undergone the expected downfield shift from those of base-free  $\text{Ph}_3\text{Al}$ . The  $^1\text{H}$  NMR spectrum of **I** contains a doublet at  $\delta$  0.11 ppm, arising from the coupling of a single  $^{31}\text{P}$  atom with the  $\text{SiMe}_3$  protons ( $^3J_{\text{P-H}} = 4.8$  Hz), indicative of an adduct structure. A doublet is also present in the  $^{13}\text{C}\{^1\text{H}\}$  solution NMR spectrum of **I** at  $\delta = 3.15$  ppm ( $^3J_{\text{P-C}} = 7.31$  Hz), which is due to the coupling of the  $\text{SiMe}_3$  carbons with the phosphorus atom. The  $^1\text{H}$  NMR spectrum of **III** contains a doublet at  $\delta$  0.17 ppm ( $^3J_{\text{P-H}} = 5.10$  Hz), due to the coupling of the P atom with the  $\text{Me}_3\text{Si}$  protons, and that of compounds **IV** and **V** contain a singlet at  $\delta$  0.19 ppm and a doublet at  $\delta$  0.26 ppm respectively. The  $^{31}\text{P}$  NMR spectra of **I**, **III**, and **V** contain only a singlet at  $\delta$  -232.5, -225.2, and -220.1 ppm respectively, which are within the range typically observed for Al-P adduct compounds.<sup>22-30,33</sup> The chemical shifts for  $\text{SiMe}_3$  protons in **II** and **IV** are in accordance with those previously observed for other Al-As Lewis acid-base adducts.<sup>31,34</sup> Compound **V** has a coupling constant  $J_{\text{P-H}} = 5.07$  Hz similar to that for **III** ( $J_{\text{P-H}} = 5.10$  Hz). The chemical shifts observed for  $^{27}\text{Al}$  NMR spectra of **I** ( $\delta$  189.5 ppm) and **III** ( $\delta$

181.6 ppm) are well within the range (120 - 220 ppm) of four coordinated aluminium centre.<sup>35</sup>

### *Conclusions*

The adducts I-V are the first examples of triphenylaluminium compounds containing heavier pnictogen atoms. The syntheses and characterization of these species reiterates the tendency for phenylaluminium derivatives to form 1:1 Lewis acid-base adducts with silylpnictines rather than elimination-condensation products.

### *Acknowledgment*

This work was funded by the office of Naval Research AASERT Program.

### *Supplementary material*

Atomic coordinates, thermal parameters, complete bond lengths and angles, and crystallographic data have been deposited with the Cambridge Crystallographic Data Centre.

## REFERENCES

1. J. F. Malone and W. S. McDonald, *Chem. Comm.* 1967, 444.
2. J. M. Burlitch, M. E. Leonowicz, R. B. Petersen and R. E. Hughes, *Inorg. Chem.* 1979, **18**, 1097.
3. M. D. B. Dillingham, S. J. Schauer, W. T. Pennington and G. H. Robinson, *J. Coord. Chem.* 1993, **30**, 19.
4. M. D. B. Dillingham, S. J. Schauer, J. Byers-Hill, W. T. Pennington and G. H. Robinson, *J. Coord. Chem.* 1994, **31**, 283.
5. M. S. Lalama, J. Kampf, D. G. Dick and J. P. Oliver, *Organometallics* 1995, **14**, 495.
6. M. Taghiof, M. J. Heeg, M. Bailey, D. G. Dick, R. Kumar, D. G. Hendershot, H. Rahbarnoohi and J. P. Oliver, *Organometallics* 1995, **14**, 2903.
7. R. Kumar, D. G. Dick, S. U. Ghazi, M. Taghiof, M. J. Heeg and J. P. Oliver, *Organometallics* 1995, **14**, 1601.
8. R. J. Wehmschulte, K. Ruhlandt-Senge and P. P. Power, *Inorg. Chem.* 1994, **33**, 3205.
9. R. L. Wells, W. K. Holley, S. Shafieezad, A. T. McPhail and C. G. Pitt, *Phosphorus, Sulfur, and Silicon* 1989, **41**, 15.
10. R. L. Wells, A. T. McPhail, L. J. Jones III, M. F. Self and R. J. Butcher, *Organometallics* 1992, **11**, 2694.
11. R. L. Wells, S. R. Aubuchon, M. F. Self, J. P. Jasinski, R. C. Woudenberg and R. J. Butcher, *Organometallics* 1992, **11**, 3370.
12. R. L. Wells, A. T. McPhail, L. J. Jones and M. F. Self, *Polyhedron* 1993, **12**, 141.
13. R. L. Wells, A. T. McPhail, L. J. Jones and M. F. Self, *Organometallics* 1992, **11**, 2694.
14. D. F. Shriver and M. A. Drezdson, *The Manipulation of Air-Sensitive Compounds*, John Wiley & Sons (New York), 1986.

15. G. Becker and W. Z. Hoelderich, *Chem. Ber.* 1975, **108**, 2484.
16. G. Becker, G. Gutekunst and H. J. Wessely, *Z. Anorg. Allg. Chem.* 1980, **462**, 113.
17. R. L. Wells, M. F. Self, J. D. Johansen, J. A. Laske, S. R. Aubuchon and L. J. Jones III, *Inorganic Syntheses* In Press.
18. E. J. Gabe, Y. Le Page, J. P. Charland, R. L. Lee and P. S. White, *J. Appl. Cryst.* 1989, **22**, 384.
19. *International Tables for X-ray Crystallography*, Kynoch (Birmingham, England), 1974.
20. W. C. Hamilton, *Acta. Cryst.* 1965, **18**, 502.
21. C. K. Johnson, *ORTEP - A Fortran Thermal Ellipsoid Plot Program*, Technical Report ORNL-5138, 1976.
22. A. Almenningen, L. Fernholt and A. Haaland, *J. Organomet. Chem.* 1978, **145**, 109.
23. G. H. Robinson, M. F. Self, S. A. Sangokoya and W. T. Pennington, *J. Crystallogr. Spectrosc.* 1988, **18**, 285.
24. M. D. Healy, D. A. Wierda and A. R. Barron, *Organometallics* 1988, **7**, 2543.
25. E. Nieke, M. Leuer and M. Nieger, *Chem. Ber.* 1989, **122**, 453.
26. D. A. Wierda and A. R. Barron, *Polyhedron* 1989, **8**, 831.
27. D. C. Bradley, H. Chudzynska, M. M. Faktor, D. M. Frigo, M. B. Hursthouse, B. Hussain and L. M. Smith, *Polyhedron* 1988, **7**, 1289.
28. S. A. Sangokoya, B. Lee, M. F. Self, W. T. Pennington and G. H. Robinson, *Polyhedron* 1989, **8**, 1497.
29. R. L. Wells, A. T. McPhail, M. F. Self and J. A. Laske, *Organometallics* 1993, **12**, 3333.
30. R. L. Wells, A. T. McPhail, J. A. Laske and P. S. White, *Polyhedron* 1994, **13**, 2737.

31. R. L. Wells, A. T. McPhail and T. M. Speer, *Eur. J. Solid State Inorg. Chem.* 1992, **29**, 63.
32. R. L. Wells, C. G. Pitt, A. T. McPhail, A. P. Purdy, S. Shafieezad and R. B. Hallock, *Mat. Res. Soc. Symp. Proc.* 1989, **131**, 45.
33. L. Rösch and W. Schmidt-Fritsche, *Z. Anorg. Allg. Chem.* 1976, **426**, 99.
34. R. L. Wells, A. T. McPhail and T. M. Speer, *Organometallics* 1992, **11**, 960.
35. R. Benn, A. Rufinska, H. Lehmkuhl, E. Janssen and C. Krüger, *Angew. Chem., Int. Ed. Engl.* 1983, **22**, 779.

Table 1. Crystallographic Data and Data Collection Parameters for  $\text{Ph}_3\text{Al}\cdot\text{P}(\text{SiMe}_3)_3$  (I),  $\text{Ph}_3\text{Al}\cdot\text{P}(\text{SiMe}_3)_3$  (II), and  $\text{Ph}_2(\text{Cl})\text{Al}\cdot\text{P}(\text{SiMe}_3)_3$  (III).

	I	II
molecular formula	$\text{C}_{27}\text{H}_{42}\text{AlPSi}_3$	$\text{C}_{27}\text{H}_{42}\text{AlAsSi}_3$
formula weight	508.83	552.80
crystal system	monoclinic	triclinic
space group	$P2_1/n (C_{2h}^5)$ - No. 14	$P\bar{1} (C_1^1)$ - No. 2
$a$ , Å	18.678(4)	16.097(2)
$b$ , Å	19.010(7)	16.254(2)
$c$ , Å	18.776(4)	12.488(2)
$\alpha$ , deg	90.0(-)	92.03(1)
$\beta$ , deg	112.49(2)	97.70(1)
$\gamma$ , deg	90.0(-)	86.85(1)
$V$ , Å <sup>3</sup>	6159(3)	3232(1)
$Z$	8	4
$D_{\text{calcd}}$ , g cm <sup>-3</sup>	1.097	1.136
$\mu$ , mm <sup>-1</sup>	0.24	.29
temp, °C	-130	25
crystal dimension, mm	0.42 x 0.30 x 0.25	0.20 x 0.24 x 0.50
$T_{\text{max}}, T_{\text{min}}$	0.94, 0.90	$T_{\text{max}}:T_{\text{min}}$ (relative) 1.00:0.83
scan type	$\omega$ -2 $\theta$	$\omega$ -2 $\theta$
$\theta_{\text{max}}$ , deg	2 $\theta$ :45	75
Total no of reflections recorded	10240(+ $h$ , + $k$ , $\pm l$ )	13784(+ $h$ , $\pm k$ , $\pm l$ )
no of non-equiv. reflections	8048	13288
$R_{\text{merge}}$ , on $I$	0.041	0.022
no of reflections retained	4834 ( $I > 2.5\sigma I$ )	7880 ( $I > 3.0\sigma I$ )
no of parameters refined	578	578
$R$ , $R_w^a$	0.048 (0.051)	0.040 (0.053)
goodness-of-fit <sup>b</sup>	1.30	1.44
max shift; esd in final least-squares cycle	0.001	0.03
final $\Delta\rho(\text{e}/\text{\AA}^3)$ max;min	0.29; -0.30	0.30; -0.74

<sup>a</sup> $R = \sum |F_O| - |F_C| / \sum |F_O|$ ;  $R_w = [\sum w(|F_O| - |F_C|)^2 / \sum w|F_O|^2]^{1/2}$ ;  $\sum w\Delta^2$  [ $w = 1/\sigma^2(|F_O|)$ ,  $\Delta = (|F_O| - |F_C|)$ ] was minimized. <sup>b</sup>Goodness-of-fit =  $[\sum w\Delta^2 / (N_{\text{observations}} - N_{\text{parameters}})]^{1/2}$ .

Table 1 (continued).

III	
molecular formula	C <sub>21</sub> H <sub>37</sub> AlClPSi <sub>3</sub>
formula weight	467.20
crystal system	orthorhombic
space group	<i>P</i> 2 <sub>1</sub> 2 <sub>1</sub> 2 <sub>1</sub> ( <i>D</i> <sub>2</sub> <sup>4</sup> )-No.19
<i>a</i> , Å	9.759(1)
<i>b</i> , Å	30.463(6)
<i>c</i> , Å	9.343(1)
$\alpha$ , deg	90.0(-)
$\beta$ , deg	90.0(-)
$\gamma$ , deg	90.0(-)
<i>V</i> , Å <sup>3</sup>	2778(1)
<i>Z</i>	4
<i>D</i> <sub>calcd</sub> , g cm <sup>-3</sup>	1.117
$\mu$ , cm <sup>-1</sup>	34.0
temp, °C	25
crystal dimension, mm	0.16 x 0.34 x 0.70
<i>T</i> <sub>max</sub> , <i>T</i> <sub>min</sub>	<i>T</i> <sub>max</sub> : <i>T</i> <sub>min</sub> (relative) 1.00:0.59
scan type	$\omega$ -2 $\theta$
$\theta$ <sub>max</sub> , deg	75
Total no of reflections recorded	3250(+ <i>h</i> , + <i>k</i> , + <i>l</i> )
no of non-equiv. reflections	3250
<i>R</i> <sub>merge</sub> , on <i>I</i>	-
no of reflections retained	2485( <i>I</i> > 3.0 $\sigma$ <i>I</i> )
no of parameters refined	244
<i>R</i> , <i>R</i> <sub>w</sub> <sup>a</sup>	0.046 (0.064)
goodness-of-fit <sup>b</sup>	1.68
max shift; esd in final least-squares cycle	0.03
final $\Delta\rho$ (e/Å <sup>3</sup> ) max;min	0.27; -0.32

<sup>a</sup> $R = \sum |F_O| - |F_C| / \sum |F_O|$ ;  $R_w = [\sum w(|F_O| - |F_C|)^2 / \sum w|F_O|^2]^{1/2}$ ;  $\sum w\Delta^2$  [ $w = 1/\sigma^2(|F_O|)$ ,  $\Delta = (|F_O| - |F_C|)$ ] was minimized. <sup>b</sup>Goodness-of-fit =  $[\sum w\Delta^2 / (N_{\text{observations}} - N_{\text{parameters}})]^{1/2}$ .

Table 2. Selected Bond Distances (Å) and Angles (deg) for  $\text{Ph}_3\text{Al}\cdot\text{P}(\text{SiMe}_3)_3$  (I), with Estimated Standard Deviations in Parentheses.

Molecule 1			
(a) Bond Lengths			
Al(1)-P(1)	2.514(2)	P(1)-Si(11)	2.282(2)
Al(1)-C(11)	1.988(5)	P(1)-Si(12)	2.282(2)
Al(1)-C(21)	1.990(5)	P(1)-Si(13)	2.281(2)
Al(1)-C(31)	1.985(6)	Si-C	1.846(7)-1.864(7)
(b) Bond Angles			
P(1)-Al(1)-C(11)	107.1(2)	Al(1)-P(1)-Si(11)	113.8(1)
P(1)-Al(1)-C(21)	107.2(2)	Al(1)-P(1)-Si(12)	110.4(1)
P(1)-Al(1)-C(31)	104.6(1)	Al(1)-P(1)-Si(13)	113.2(1)
C(11)-Al(1)-C(21)	110.5(2)	Si(11)-P(1)-Si(12)	106.7(1)
C(11)-Al(1)-C(31)	113.0(2)	Si(11)-P(1)-Si(13)	105.9(1)
C(21)-Al(1)-C(31)	113.9(2)	Si(12)-P(1)-Si(13)	106.4(1)
(c) Torsion Angles <sup>a</sup>			
Si(11)-P(1)-Al(1)-C(11)	-94.4(2)	Si(13)-P(1)-Al(1)-C(31)	146.7(2)
Si(11)-P(1)-Al(1)-C(21)	147.0(2)	P(1)-Al(1)-C(11)-C(12)	-129.8(4)
Si(11)-P(1)-Al(1)-C(31)	25.8(2)	P(1)-Al(1)-C(21)-C(22)	-112.3(5)
Si(12)-P(1)-Al(1)-C(11)	145.7(2)	P(1)-Al(1)-C(31)-C(32)	-112.2(3)
Si(12)-P(1)-Al(1)-C(21)	27.1(2)	Al(1)-P(1)-Si(11)-C(111)	41.7(2)
Si(12)-P(1)-Al(1)-C(31)	-92.1(2)	Al(1)-P(1)-Si(12)-C(121)	45.3(2)
Si(13)-P(1)-Al(1)-C(11)	26.6(2)	Al(1)-P(1)-Si(13)-C(131)	37.4(2)
Si(13)-P(1)-Al(1)-C(21)	-94.1(2)		

Table 2 (continued).

---

Molecule 2			
(a) Bond Lengths			
Al(2)-P(2)	2.521(2)	P(2)-Si(21)	2.285(2)
Al(2)-C(41)	1.990(5)	P(2)-Si(22)	2.288(2)
Al(2)-C(51)	1.989(6)	P(2)-Si(23)	2.283(2)
Al(2)-C(61)	1.991(6)	Si-C	1.847(7)-1.863(6)
(b) Bond Angles			
P(2)-Al(2)-C(41)	105.5(2)	Al(2)-P(2)-Si(21)	114.1(1)
P(2)-Al(2)-C(51)	106.2(2)	Al(2)-P(2)-Si(22)	110.1(1)
P(2)-Al(2)-C(61)	104.9(2)	Al(2)-P(2)-Si(23)	113.5(1)
C(41)-Al(1)-C(51)	111.2(2)	Si(21)-P(2)-Si(22)	107.0(1)
C(41)-Al(1)-C(61)	114.5(2)	Si(21)-P(2)-Si(23)	105.7(1)
C(51)-Al(1)-C(61)	113.6(3)	Si(22)-P(2)-Si(23)	106.0(1)
(c) Torsion Angles <sup>a</sup>			
Si(21)-P(2)-Al(2)-C(41)	-96.6(2)	Si(23)-P(2)-Al(2)-C(61)	145.8(2)
Si(21)-P(2)-Al(2)-C(51)	145.3(2)	P(2)-Al(2)-C(41)-C(42)	-122.6(4)
Si(21)-P(2)-Al(2)-C(61)	24.7(2)	P(2)-Al(2)-C(51)-C(52)	-114.0(4)
Si(22)-P(2)-Al(2)-C(41)	143.1(2)	P(2)-Al(2)-C(61)-C(62)	-114.3(4)
Si(22)-P(2)-Al(2)-C(51)	24.9(2)	Al(2)-P(2)-Si(21)-C(211)	42.2(2)
Si(22)-P(2)-Al(2)-C(61)	-95.7(2)	Al(2)-P(2)-Si(22)-C(221)	43.5(2)
Si(23)-P(2)-Al(2)-C(41)	24.5(2)	Al(2)-P(2)-Si(23)-C(231)	38.8(2)
Si(23)-P(2)-Al(2)-C(51)	-93.6(2)		

---

<sup>a</sup>The torsion angle A-B-C-D is defined as positive if, when viewed along the B-C bond, atom A must be rotated clockwise to eclipse atom D.

Table 3. Selected Bond Distances (Å) and Angles (deg) for  $\text{Ph}_3\text{Al}\cdot\text{As}(\text{SiMe}_3)_3$  (II), with Estimated Standard Deviations in Parentheses.

Molecule 1			
(a) Bond Lengths			
As-Al	2.598(1)	Al-C(11)	1.989(4)
As-Si(11)	2.382(1)	Al-C(21)	1.979(4)
As-Si(12)	2.376(1)	Al-C(31)	1.987(3)
As-Si(13)	2.379(1)	Si-C	1.851(6)-1.863(5)
(b) Bond Angles			
Al-As-Si(11)	112.53(4)	As-Al-C(11)	105.2(1)
Al-As-Si(12)	113.18(4)	As-Al-C(21)	102.9(1)
Al-As-Si(13)	112.91(4)	As-Al-C(31)	105.3(1)
Si(11)-As-Si(12)	104.77(4)	C(11)-Al-(21)	114.1(2)
Si(11)-As-Si(13)	106.78(4)	C(11)-Al-C(31)	114.0(2)
Si(12)-As-Si(13)	106.04(5)	C(21)-Al-C(31)	113.9(2)
(c) Torsion Angles <sup>a</sup>			
Si(11)-As-Al-C(11)	-91.5(1)	Si(13)-As-Al-C(31)	-91.2(1)
Si(11)-As-Al-C(21)	28.2(1)	As-Al-C(11)-C(12)	65.5(3)
Si(11)-As-Al-C(31)	147.8(1)	As-Al-C(21)-C(22)	72.8(3)
Si(12)-As-Al-C(11)	150.0(1)	As-Al-C(31)-C(36)	62.9(4)
Si(12)-As-Al-C(21)	-90.3(1)	Al-As-Si(11)-C(113)	42.4(2)
Si(12)-As-Al-C(31)	29.2(1)	Al-As-Si(12)-C(122)	41.7(2)
Si(13)-As-Al-C(11)	29.5(1)	Al-As-Si(13)-C(131)	39.2(2)
Si(13)-As-Al-C(21)	149.2(1)		
Molecule 2			
(a) Bond Lengths			
As'-Al'	2.613(1)	Al'-C(11')	1.985(5)
As'-Si(11')	2.371(1)	Al'-C(21')	1.994(4)
As'-Si(12')	2.382(1)	Al'-C(31')	1.980(3)
As'-Si(13')	2.372(1)	Si-C	1.846(6)-1.865(6)

Table 3 (continued).

## (b) Bond Angles

---

Al'-As'-Si(11')	111.88(4)	As'-Al'-C(11')	103.4(1)
Al'-As'-Si(12')	112.91(4)	As'-Al'-C(21')	105.5(1)
Al'-As'-Si(13')	113.37(5)	As'-Al'-C(31')	104.9(1)
Si(11')-As'-Si(12')	106.23(5)	C(11')-Al'-C(21')	115.0(2)
Si(11')-As'-Si(13')	105.40(5)	C(11')-Al'-C(31')	114.3(2)
Si(12')-As'-Si(13')	106.46(5)	C(21')-Al'-C(31')	112.4(2)

(c) Torsion Angles<sup>a</sup>

Si(11')-As'-Al'-C(11')	-96.8(2)	Si(13')-As'-Al'-C(31')	-97.9(1)
Si(11')-As'-Al'-C(21')	24.2(1)	As'-Al'-C(11')-C(12')	73.8(4)
Si(11')-As'-Al'-C(31')	143.1(1)	As'-Al'-C(21')-C(22')	66.3(3)
Si(12')-As'-Al'-C(11')	143.4(1)	As'-Al'-C(31')-C(36')	61.4(4)
Si(12')-As'-Al'-C(21')	-95.6(1)	Al'-As'-Si(11')-C(113')	38.6(2)
Si(12')-As'-Al'-C(31')	23.3(1)	Al'-As'-Si(12')-C(122')	38.4(2)
Si(13')-As'-Al'-C(11')	22.2(1)	Al'-As'-Si(13')-C(131')	46.1(2)
Si(13')-As'-Al'-C(21')	143.2(1)		

---

<sup>a</sup>The torsion angle A-B-C-D is defined as positive if, when viewed along the B-C bond, atom A must be rotated clockwise to eclipse atom D.

Table 4. Selected Bond Distances (Å) and Angles (deg) for  $\text{Ph}_2(\text{Cl})\text{Al}\cdot\text{P}(\text{SiMe}_3)_3$  (III), with Estimated Standard Deviations in Parentheses.

(a) Bond Lengths

Al-Cl	2.173(2)	P-Si(1)	2.284(2)
Al-P	2.467(2)	P-Si(2)	2.285(1)
Al-C(1a)	1.968(5)	P-Si(3)	2.283(2)
Al-C(1b)	1.989(6)	Si-C	1.841(8)-1.879(6)

(b) Bond Angles

Cl-Al-P	102.1(1)	Al-P-Si(1)	108.6(1)
Cl-Al-C(1a)	109.7(2)	Al-P-Si(2)	110.7(1)
Cl-Al-C(1b)	110.1(2)	Al-P-Si(3)	114.4(1)
P-Al-C(1a)	109.0(2)	Si(1)-P-Si(2)	108.4(1)
P-Al-C(1b)	109.3(2)	Si(1)-P-Si(3)	107.5(1)
C(1a)-Al-C(1b)	115.7(2)	Si(2)-P-Si(3)	107.1(1)

(c) Torsion Angles<sup>a</sup>

Si(1)-P-Al-Cl	79.0(1)	Si(3)-P-Al-C(1b)	-44.4(2)
Si(1)-P-Al-C(1a)	-37.1(2)	P-Al-C(1a)-C(2a)	104.8(4)
Si(1)-P-Al-C(1b)	-164.5(2)	P-Al-C(1b)-C(2b)	82.0(4)
Si(2)-P-Al-Cl	-39.9(1)	Al-P-Si(1)-C(11)	-42.4(3)
Si(2)-P-Al-C(1a)	-155.9(2)	Al-P-Si(2)-C(21)	-45.5(3)
Si(2)-P-Al-C(1b)	76.7(2)	Al-P-Si(3)-C(32)	-42.7(2)
Si(3)-P-Al-Cl	-161.0(2)	Cl-Al-C(1a)-C(2a)	-6.3(5)
Si(3)-P-Al-C(1a)	83.0(2)	Cl-Al-C(1b)-C(6b)	-2.2(5)

<sup>a</sup>The torsion angle A-B-C-D is defined as positive if, when viewed along the B-C bond, atom A must be rotated clockwise to eclipse atom D.

### CAPTIONS TO FIGURES

Figure 1. Thermal ellipsoid diagrams (40% probability) showing the solid state conformation and atom numbering scheme of  $\text{Ph}_3\text{Al}\cdot\text{P}(\text{SiMe}_3)_3$  (**I**) (molecule 1) in the asymmetric crystal unit; hydrogen atoms have been omitted for clarity.

Figure 2. Thermal ellipsoid diagrams (40% probability) showing the solid state conformation and atom numbering scheme of  $\text{Ph}_3\text{Al}\cdot\text{As}(\text{SiMe}_3)_3$  (**II**) (molecule 1) in the asymmetric crystal unit; hydrogen atoms have been omitted for clarity.

Figure 3. A thermal ellipsoid diagram (40% probability) showing the solid state conformation and atom numbering scheme of  $\text{Ph}_2(\text{Cl})\text{Al}\cdot\text{P}(\text{SiMe}_3)_3$  (**III**); small circles represent hydrogen atoms.

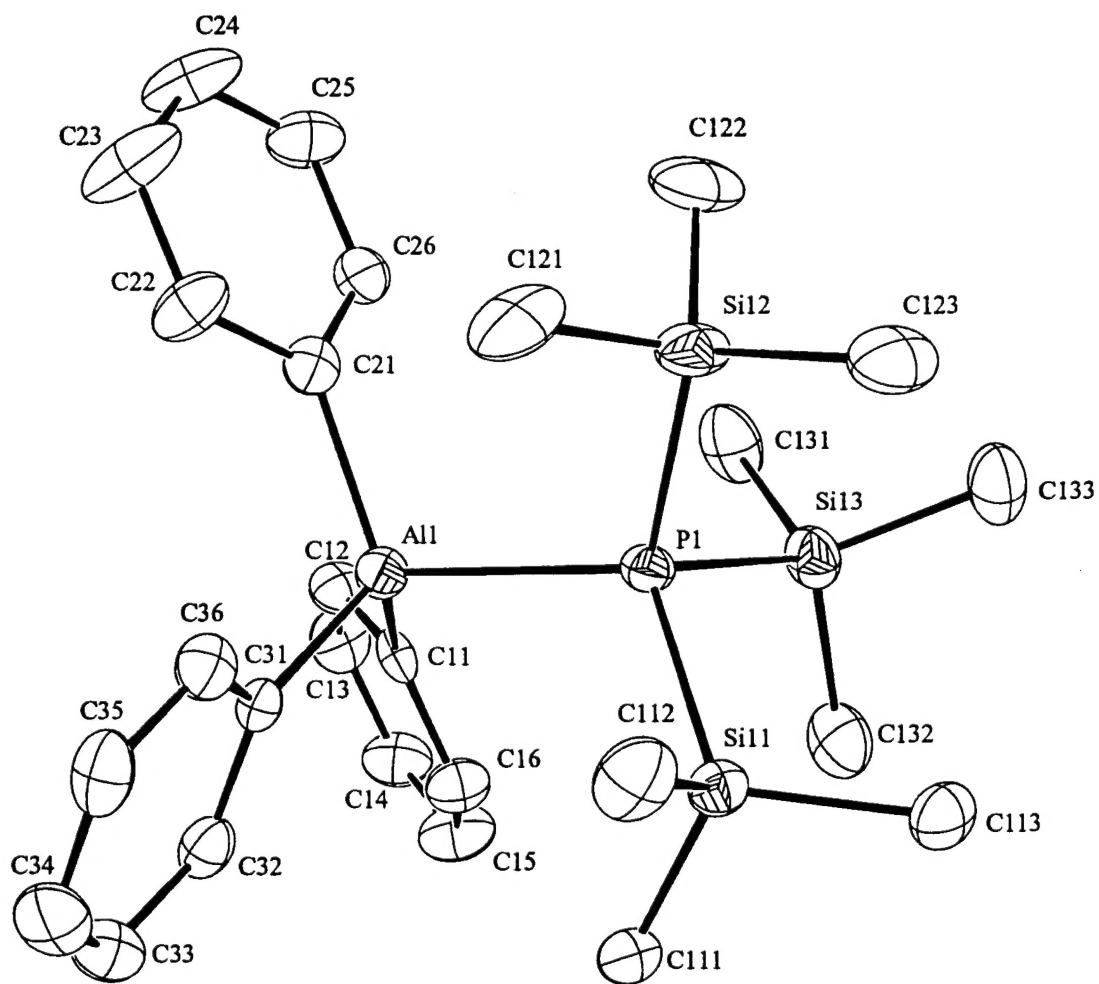


Figure 1

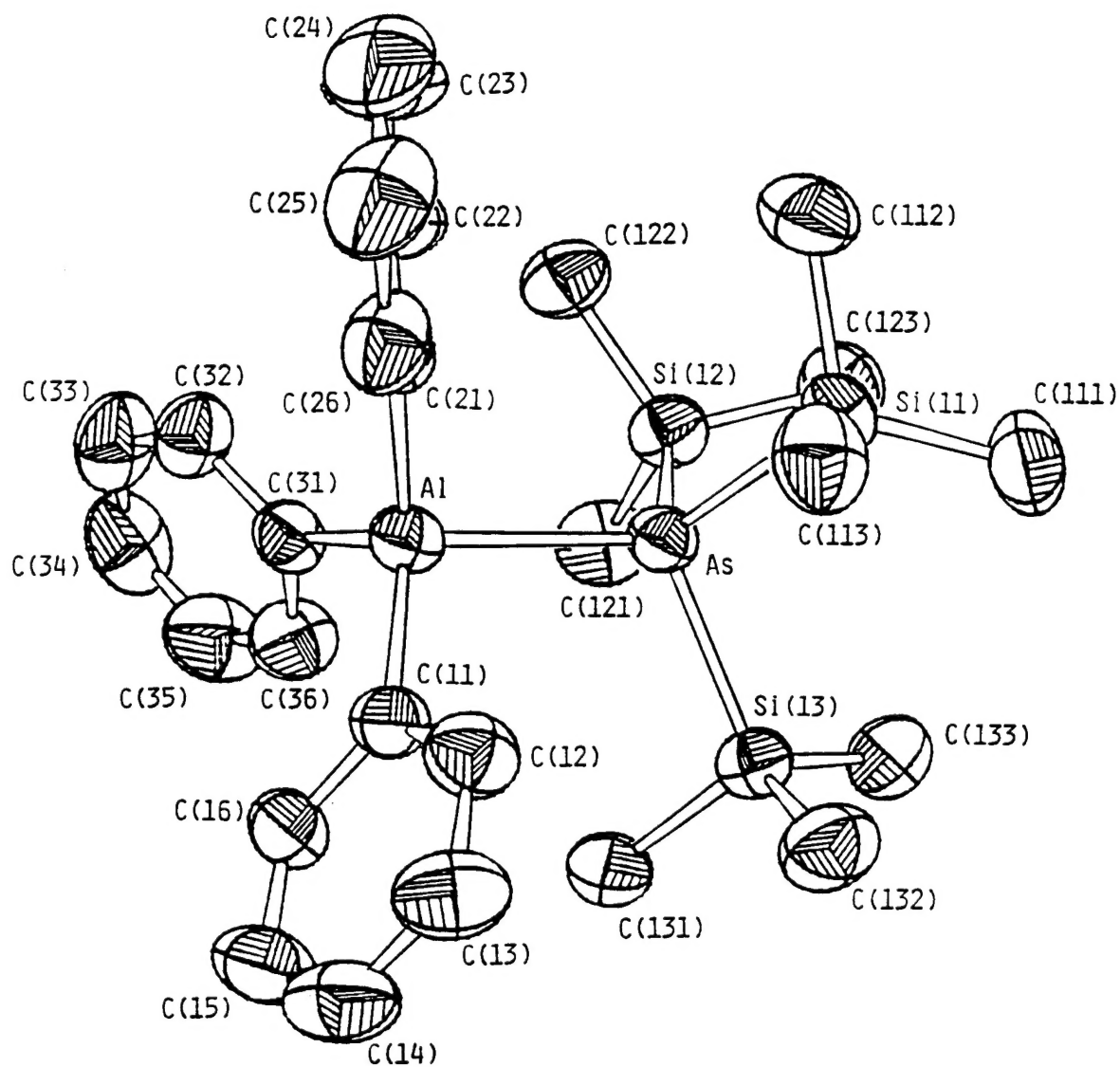


Figure 2

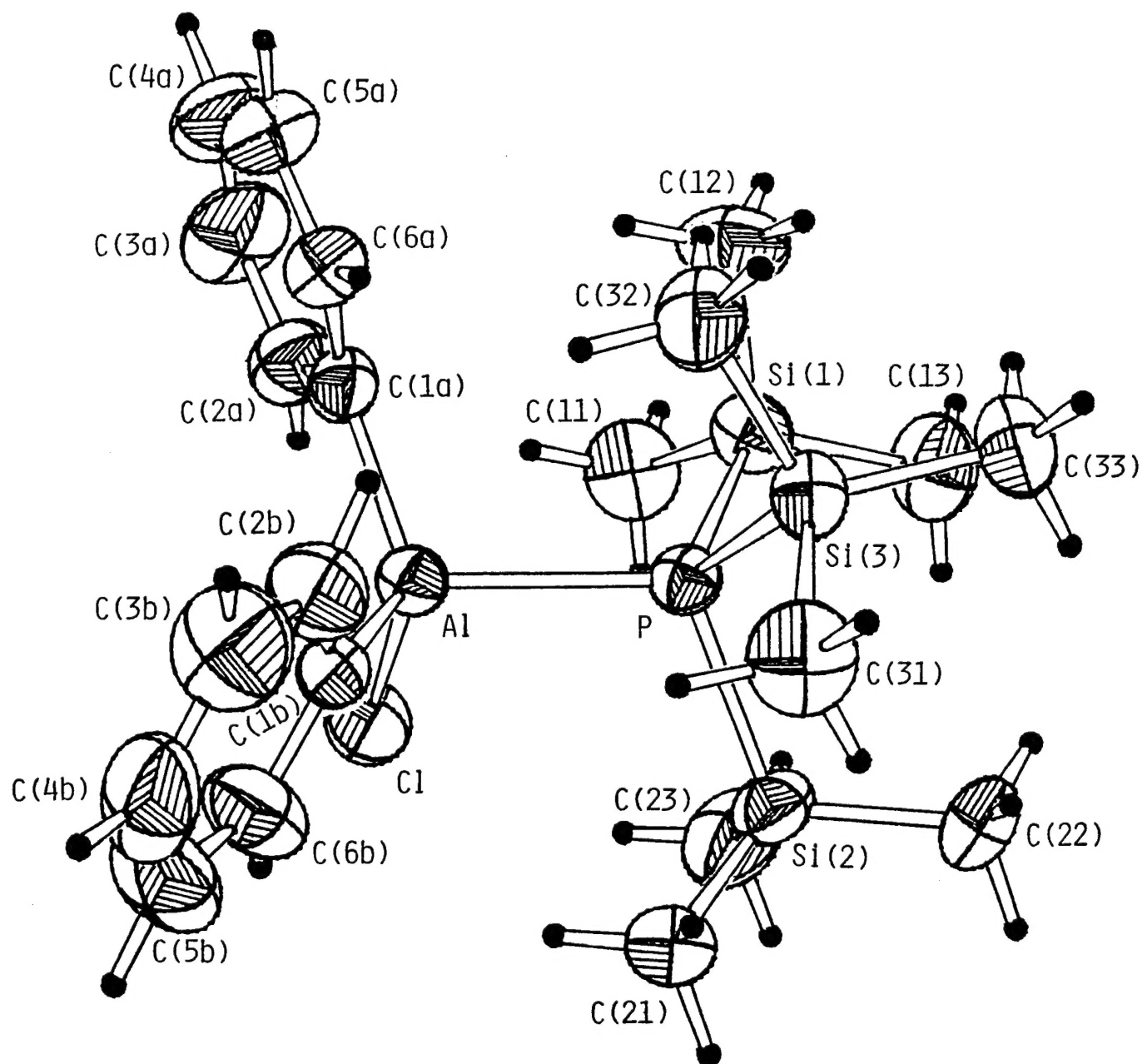


Figure 3

TECHNICAL REPORT DISTRIBUTION LIST - GENERAL

Office of Naval Research (1)\*  
Chemistry Division, ONR 331  
800 North Quincy Street  
Arlington, Virginia 22217-5660

Dr. Richard W. Drisko (1)  
Naval Facilities & Engineering  
Service Center  
Code L52  
Port Hueneme, CA 93043

Defense Technical Information  
Center (2)  
Building 5, Cameron Station  
Alexandria, VA 22314

Dr. Eugene C. Fischer (1)  
Code 2840  
Naval Surface Warfare Center  
Carderock Division Detachment  
Annapolis, MD 21402-1198

Dr. James S. Murday (1)  
Chemistry Division, Code 6100  
Naval Research Laboratory  
Washington, D.C. 20375-5320

Dr. Bernard E. Douda (1)  
Crane Division  
Naval Surface Warfare Center  
Crane, Indiana 47522-5000

Dr. John Fischer, Director (1)  
Chemistry Division, C0235  
Naval Air Weapons Center  
Weapons Division  
China Lake, CA 93555-6001

Dr. Peter Seligman (1)  
Naval Command, Control and  
Ocean Surveillance Center  
RDT&E Division  
San Diego, CA 92152-5000

\* Number of copies to forward